SN 10/540,528

JAPAN PATENT OFFICE

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Date of Application: December 27, 2002

Application Number: JP2002-381563

Applicant(s): Daicel Chemical Industries, Ltd.

February 5, 2004

Commissioner,

Japan Patent Office Yasuo Imai

【Document】 Request for Patent
【Docket No.】 024019
【Date of Application】 December 27, 2002
【Address】 Commissioner, Patent Office
【International Patent Classification】
C08G 59/20
C09D 4/00
G11B 7/24
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【Payment of Fees】
【Deposit Account No.】 026033
【Amount to be paid】 21,000
【Attached Documents】
【Item】 Specification one copy
【Item】 Abstract one copy
【General Power of Attorney No.】
9402017
【Necessity of Proof】 needed

【Document】 Specification

【Title】 CURABLE RESIN COMPOSITION AND PRODUCTS OF CURING THEREOF

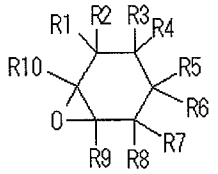
【Claims】

【Claim 1】

A heat-curable resin composition comprising an alicyclic epoxy compound (a) having a structure represented by the following general formula (1),

【Chemical Formula 1】

General formula (1)



[In the general formula (1): R^1 to R^{10} each represent hydrogen, or a saturated or unsaturated hydrocarbon group having 1 to 20 carbon atoms (an ether bond, an ester bond, or an alcoholic hydroxyl group may be included in the hydrocarbon group); R^1 to R^{10} may each represent a residue derived by removing any one of R^1 to R^{10} from the structure represented by the general formula (1), or a residue derived by removing hydrogen from any one of R^1 to R^{10}; and the phrase "in the hydrocarbon group" refers to "inside the hydrocarbon group", "at terminals of the hydrocarbon group", or "within bonds of the hydrocarbon group"], a cationic polymerization initiator (i), and optionally a surfactant (e).

【Claim 2】

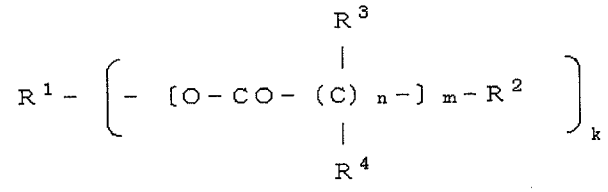
A heat-curable resin composition according to claim 1, further comprising a polyol (b) having two or more hydroxyl groups on terminals.

【Claim 3】

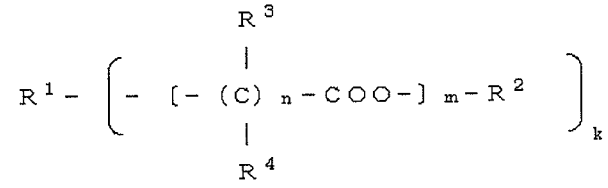
A heat-curable resin composition comprising an alicyclic epoxy compound (a') having a structure represented by the following general formula (2),

【Chemical Formula 2】

general formula (2)



or

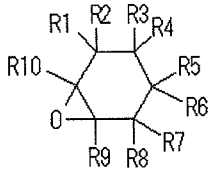


[In the general formula (2): R^1 represents hydrogen, or a hydrocarbon group of a valence k having 1 to 20 carbon atoms (an ether bond, an ester bond, or an alcoholic hydroxyl group may be included in the hydrocarbon group); R^2 represents hydrogen, a hydroxyl group, or a hydrocarbon group having 1 to 20 carbon atoms (an ether bond, an ester bond, or an alcoholic hydroxyl group may be included in the hydrocarbon group); at least one of R^1 and R^2 may represent a residue derived by removing any one of R^1 to R^{10} from the structure

represented by the following general formula (1); R^3 and R^4 each represents hydrogen, or a hydrocarbon group having 1 to 20 carbon atoms; a plurality of R^3s and R^4s may be the same or different from each other; "n" represents an integer of 3 to 10; "m" represents an integer of 2 to 10; "k" represents an integer of 1 to 10; when "k" is 2 or more, "k" pieces of group structures may be the same or different from each other; and the phrase "in the hydrocarbon group" refers to "inside the hydrocarbon group", "at terminals of the hydrocarbon group", or "within bonds of the hydrocarbon group"],

【Chemical Formula 3】

General formula (1)



[In the general formula (1): R^1 to R^{10} each represent hydrogen, or a saturated or unsaturated hydrocarbon group having 1 to 20 carbon atoms (an ether bond, an ester bond, or an alcoholic hydroxyl group may be included in the hydrocarbon group); R^1 to R^{10} may each represent a residue derived by removing any one of R^1 to R^{10} from the structure represented by the general formula (1), or a residue derived by removing hydrogen from any one of R^1 to R^{10}; and the phrase "in the hydrocarbon group" refers to "inside the hydrocarbon group", "at terminals of the hydrocarbon group", or "within

bonds of the hydrocarbon group"], a cationic polymerization initiator (i), and optionally a surfactant (e).

【Claim 4】

A curable-resin composition according to any one of claims 1 to 3, characterized in that the surfactant (e) comprises a silicon-based surfactant (e1) having a dimethylsiloxane skeleton and/or a fluorine-based surfactant (e2) having hydrophobic groups of a hydrocarbon-based surfactant entirely or partially substituted with fluorine atoms.

【Claim 5】

A cured product, which is obtained by heat curing the heat-curable resin composition according to any one of claims 1 to 4.

【Claim 6】

A cured product according to claim 5, which is used for an adhesive or an encapsulant.

【Claim 7】

A cured product according to claim 5 or 6, wherein a warping by shrinkage in curing is 15 mm or less through a measurement method A, 6 mm or less through a measurement method B.

【Detailed Description of The Invention】

【0001】

【Technical Field】

The present invention relates to a heat-curable resin composition and a heat-cured product of the composition. The present invention more specifically relates to a useful material serving as an adhesive or insulating encapsulant used for assembly of optical parts or electronic parts requiring precise positional accuracy because the cured product has low shrinkability in curing.

【0002】

【Background Art】

Various curable resin compositions have been heretofore used as adhesives, encapsulants, and the like, and have been changed to solvent free-type curable resin compositions. However, a system involving radical polymerization of an acrylic compound has problems such as insufficient curability due to polymerization inhibition by oxygen and strong monomer odor.

【0003】

Thus, JP-A-11-302358 discloses a photocurable composition containing at least a photocationically polymerizable compound and a photoacid generator, in which a photocurable composition containing the photocationically polymerizable compound including 50 to 100% by weight of a bisphenol A-type epoxy resin and 0 to 50% by weight of a diluent has a shrinkage ratio in curing of less than 10% (Refer to Patent Document 1).

Further, JP-A-11-12495 discloses a UV-curable composition for an optical disc containing 5% by weight or more of urethane (meth)acrylate and having a shrinkage ratio in curing of 8.5% or less (Refer to Patent Document 2).

JP-A-2002-256058 discloses that an acrylic UV-curable resin has a high shrinkage ratio in curing of 10% or more (Refer to Patent Document 3).

A method of reducing shrinkage ratio in curing of a curable resin composition involves mixing of an inorganic additive. However, the addition of the inorganic additive may not only degrade smoothness of a resin surface but also cause strength reduction of the resin.

An epoxy resin has such a feature that it provides excellent heat resistance and low shrinkage in curing compared with those of other curable resins. Even very low shrinkage in curing may cause crack formation in a cured product or deformation of adherent substances, and thus the epoxy resin is not appropriate for uses requiring dimensional stability at high precision.

【0004】

However, the above-described reports each refer to a photocurable resin, and the photocurable resin has disadvantages in that it generally has poor reactivity and cannot be used for a molded product with a complicated shape which cannot be subjected to light. Thus, heat curing is

desired for obtaining a complicated molded product.

Of epoxy compounds, an alicyclic epoxy compound is used for electrical materials because a cured product having a high glass transition point (Tg) is obtained and the alicyclic epoxy compound has a small chlorine content.

Further, the alicyclic epoxy compound has such a feature that it cures in a short period of time by mixing a heat cationic polymerization initiator and heating the mixture. However, a cured product obtained through heat cationic polymerization of the alicyclic epoxy resin has disadvantages in that shrinkage in curing takes places. Further, warping, cracking, peeling, and the like are easily caused by internal stress generated from shrinkage in curing, and thus the cured product is hardly used in fields requiring precise adhesion and the like.

【0005】

JP-A-08-188702 focuses on thermal expansion property of a cyanate resin, and discloses that a cured product obtained through heat curing of a curable composition including the cyanate resin, bisphenol A, a bisphenol A-type epoxy resin, and methyl ethyl ketone has very low shrinkage in curing (Refer to Patent Document 4). However, the curable composition contains a solvent, and low shrinkage in curing was desired for a solvent free curable composition.

【0006】

【Patent Document 1】

Unexamined Japanese Patent Publication Hei 11-302358 (claims 1 to 4, paragraph 0012, Table 1)

【Patent Document 2】

Unexamined Japanese Patent Publication Hei 11-12495 (claims 1 and 2, paragraph 0016, Example 1)

【Patent Document 3】

Unexamined Japanese Patent Publication 2002-256058 (paragraph 0005)

【Patent Document 4】

Unexamined Japanese Patent Publication Hei 08-188702 (claims 1 to 6, paragraphs 0015 and 0016, Examples)

【0007】

【Technical Problem】

An object of the present invention is to provide a heat-curable resin composition which is heat-curable and is capable of providing a cured product with low shrinkage in curing.

【0008】

【Technical Solution】

The inventor of the present invention has conducted extensive studies to solve the above-described problems. As a result, the inventor of the present invention has applied a composition including an alicyclic epoxy compound, a polyol,

and a surfactant onto a flexible film, and formed a coating film through heat cationic polymerization. Thus, the inventor of the present invention has found that warping of the flexible film having the coating film formed thereon is significantly improved, and that warping of the flexible film significantly improves even in a cured product obtained through heat cationic polymerization of an alicyclic epoxy compound having a polyester chain in a molecule, to thereby complete the present invention.

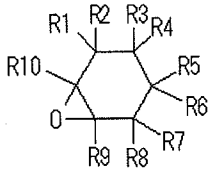
【0009】

That is, a first aspect of the present invention provides a heat-curable resin composition including an alicyclic epoxy compound (a) having a structure represented by the following general formula (1), a cationic polymerization initiator (i), and optionally a surfactant (e).

【0010】

【Chemical Formula 4】

General formula (1)



【0011】

[In the general formula (1): R^1 to R^{10} each represent hydrogen, or a saturated or unsaturated hydrocarbon group having 1 to 20 carbon atoms (an ether bond, an ester bond,

or an alcoholic hydroxyl group may be included in the hydrocarbon group); R^1 to R^{10} may each represent a residue derived by removing any one of R^1 to R^{10} from the structure represented by the general formula (1), or a residue derived by removing hydrogen from any one of R^1 to R^{10} ; and the phrase "in the hydrocarbon group" refers to "inside the hydrocarbon group", "at terminals of the hydrocarbon group", or "within bonds of the hydrocarbon group"]

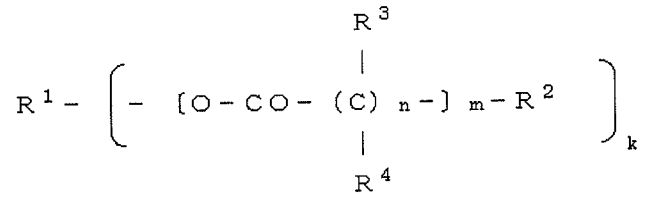
A second aspect of the present invention provides a heat-curable resin composition according to the first aspect of the present invention, further including a polyol (b) having two or more hydroxyl groups on terminals.

A third aspect of the present invention provides a heat-curable resin composition including an alicyclic epoxy compound (a') having a structure represented by the following general formula (2), a cationic polymerization initiator (i), and optionally a surfactant (e).

【0012】

【Chemical Formula 5】

general formula (2)



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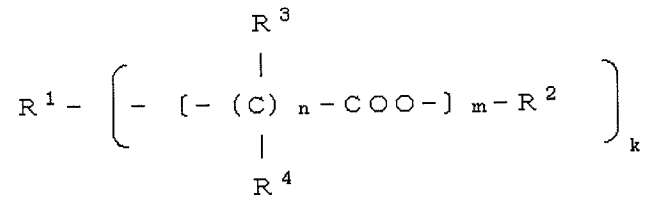

【0013】

[In the general formula (2): R^1 represents hydrogen, or a hydrocarbon group of a valence K having 1 to 20 carbon atoms, and an ether bond, an ester bond, or an alcoholic hydroxyl group may be included in the hydrocarbon group; R^2 represents hydrogen, a hydroxyl group, or a hydrocarbon group having 1 to 20 carbon atoms, and an ether bond, an ester bond, or an alcoholic hydroxyl group may be included in the hydrocarbon group; at least one of R^1 and R^2 may represent a residue derived by removing any one of R^1 to R^{10} from the structure represented by the general formula (1); R^3 and R^4 each represents hydrogen, or a hydrocarbon group having 1 to 20 carbon atoms, preferably hydrogen or a methyl group; a plurality of R^3s and R^4s may be the same or different from each other; "n" represents an integer of 3 to 10; "m" represents an integer of 2 to 10; "k" represents an integer of 1 to 10; when k is 2 or more, k group structures may be the same or different from each

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